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The surface terminal layer and composition of the colossal magnetoresistance perovskite: $La_{0.65}Pb_{0.35}MnO_3$

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The composition in the surface region of the colossal magnetoresistance perovskite manganite materials, $La_{0.65}Pb_{0.35}MnO_3$ has been studied using angle resolved x-ray photoemission spectroscopy. The results are consistent with a Mn–O terminal layer and Pb segregation to the near-surface region. This is similar to the behavior exhibited by $La_{0.65}Ca_{0.35}MnO_3$ and $La_{0.65}Sr_{0.35}MnO_3$. The O–Mn–O terminal layer appears to be close to the Mn^{3+} valence state.
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I. INTRODUCTION

The colossal magnetoresistance (CMR) perovskite transition metal oxides, $La_{0.65}A_{0.35}MnO_3$ (A=Ca, Sr, Ba)[1,2] have been studied extensively, but the related $La_{1-x}Pb_xMnO_3$ has attracted only modest attention.[3–7] In view of the fact that Pb will readily adopt several different valence states, unlike the alkaline earths, a comparison between the different $La_{0.65}A_{0.35}MnO_3$ (A=Ca, Sr, Ba, Pb) doping systems is important.[6,7] Furthermore, it is possible that different dopants will affect the surface enthalpy differently[8,9] and, consequently, the surface electronic structure and/or surface composition.

The termination layer of the perovskite manganese oxides, $La_{1-x}A_xMnO_3$ (A=Ca, Sr, Ba; $x=0.1,0.35$) has been studied using angle resolved x-ray photoemission spectroscopy,[8–10] ion scattering spectroscopy,[11,12] and angle-resolved photoemission.[13–15] The termination layer of $La_{1-x}A_xMnO_3$, with $x=0.35$, has been consistently determined to be at least partly Mn–O.[8–15] Unfortunately, because the surface free energy is expected to be different with the bulk, surface segregation is expected and has been routinely observed in some manganese perovskite oxides.[8–10,16,17] This paper explores whether $La_{0.65}Pb_{0.35}MnO_3$ exhibits a similar surface composition to $La_{0.65}A_{0.35}MnO_3$ (A=Ca, Sr, Ba) thus has a similar surface free enthalpy.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The crystalline samples with a nominal thickness of 1000 Å were grown on (100) $LaAlO_3$ substrates by rf sputtering in a 4:1 argon/oxygen atmosphere at 15 mTorr with the substrate maintained at a temperature of 300 K. The films were annealed at 650 °C for 10 h and 850 °C for 2 h in an oxygen atmosphere maintained at a pressure of 1 atm (this is less annealing than used for the alkaline doped earth manganese perovskites because of lead evaporation). The bulk chemical composition of the films was determined from energy dispersive analysis of x-ray emission spectroscopy (XES or EDAX) and found to be similar to the targets with the final compositions $La_{0.65}Pb_{0.35}MnO_3$. SQUID measurements of the sample magnetization variation with temperature indicate a Curie temperature of 350 K. The crystallinity and orientation was established by x-ray diffraction. The samples were further characterized by temperature dependence magnetoresistance. The peak temperature of resistivity versus temperature curve shifted to 420 K at a 5.5 T magnetic field, and a negative relative magnetoresistance of 47% was observed at 320 K in this field. Figure 1 shows both the zero field and high field (5.5 T) resitivities (left-hand side

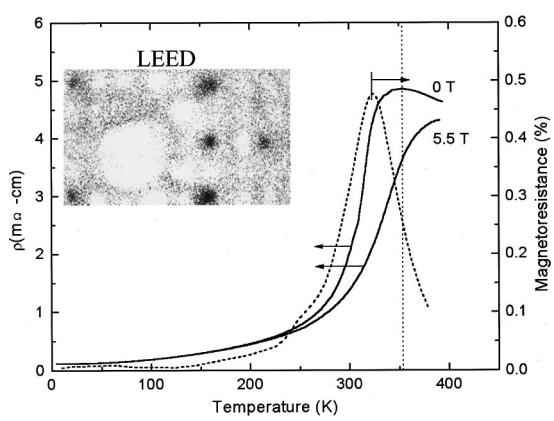

FIG. 1. The measured magnetoresistance (right-hand side axis) and resistivity as a function of temperature at zero field and high field (5.5 T) (left-hand side axis), for the 1 μm thick film. The inset shows the fourfold symmetry of the electron diffraction spots, obtained by LEED.

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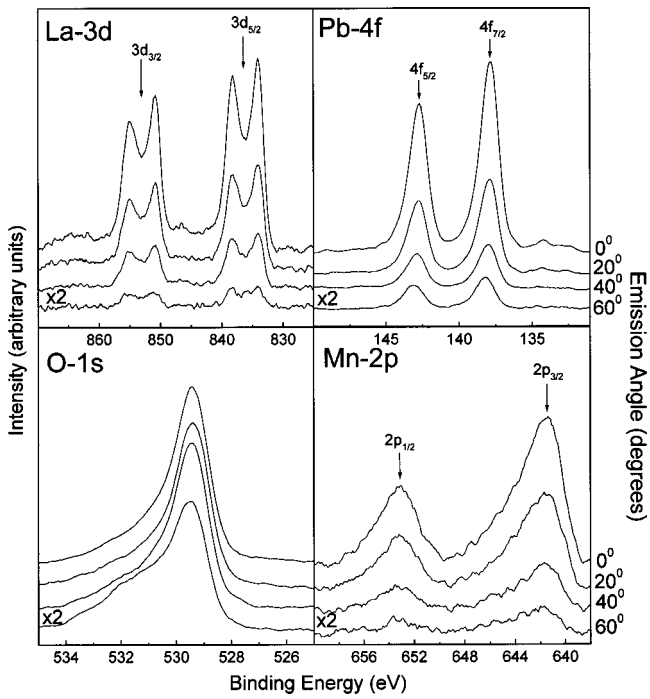

FIG. 2. The x-ray photoemission spectra of the La $3d$, Pb $4f$, O $1s$, and Mn $2p$ core levels of $La_{0.65}Pb_{0.35}MnO_3$. The spectra were taken as a function of emission angle of the photoelectron and plotted as a function of binding energy.

axis) as well as the variation of magnetoresistance (MR) as a function of temperature (right-hand side axis).

X-ray photoemission spectroscopy was undertaken with the Mg $K\alpha$ line (1253.6 eV) from a PHI Model 04-548 Dual Anode x-ray source. Energy distribution curves of the elemental core levels were acquired with a large hemispherical electron energy analyzer (PHI Model 10-360 Precision Energy Analyzer). The Fermi level was established from tantalum in electrical contact with the sample. The binding energy of core levels is reported with respect to this Fermi level and the emission angle with respect to the surface normal. Sample surfaces were cleaned in ultrahigh vacuum by repeated annealing and exposure to low energy electrons to stimulate the desorption of contaminants as described elsewhere.[14]

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Core level photoemission data are shown for $La_{0.65}Pb_{0.35}MnO_3$ in Fig. 2. Both the core level binding energies and peak shapes are similar to that reported previously for $La_{1-x}Ca_xMnO_{2.97}$ (by Choi *et al.*[18] and Taguchi and Shimada[19]) and for $La_{1-x}Sr_xMnO_3$ (Choi *et al.*[18] and Saitoh *et al.*[20]). The core level data generally suggest that the O–Mn–O layers in $La_{0.65}Pb_{0.35}MnO_3$ have fewer defects than is the case for $La_{0.65}A_{0.35}MnO_3$ (A=Ca, Sr) consistent with the better low energy electron diffraction (LEED) pattern obtained from $La_{0.65}Pb_{0.35}MnO_3$ than is the case for $La_{0.65}A_{0.35}MnO_3$ (A=Ca, Sr).[9,10,14,21] The LEED pattern is shown as an inset in Fig. 1 and it shows the approximate fourfold symmetry of the film's surface.

The oxygen core level can provide indications of the presence of defects in the manganese perovskites.[18] As shown in Fig. 2, the oxygen $1s$ core level of the perovskite manganese oxide $La_{0.65}Pb_{0.35}MnO_3$, exhibits one dominant peak at a binding energy of 529.4 eV and a shoulder at higher binding energies. This is very similar to other manganese perovskites.[18] The higher binding energy O $1s$ peak found at 531.3 eV, in the perovskites, has been attributed to either a different surface oxide or to oxygen associated with defects in the perovskite structure though exact nature of the oxygen species giving rise to this 531.3 eV feature has not yet been determined.[18] Compared to the other manganese perovskites, in $La_{0.65}Pb_{0.35}MnO_3$, this satellite feature is quite weak.

The Mn $2p$ spectra from the $La_{0.65}Pb_{0.35}MnO_3$ sample indicates that the disorder in the surface region is not as significant as in many other manganese perovskites.[18] The full width at half maximum (FWHM) of the Mn $2p$ core level spectra is about 4 eV as compared to 4–4.5 eV for $La_{0.65}Ca_{0.35}MnO_3$ and $La_{0.65}Sr_{0.35}MnO_3$.[18] The relatively narrow Mn $2p$ half width is consistent with the restriction of Mn to a single valence state and an absence of significant numbers of defects in the surface region. The Mn $3p_{3/2}$ core level binding energies (shown in Fig. 2) of 641.5 eV for $La_{0.65}Pb_{0.35}MnO_3$ is very similar to that observed for Mn_3O_4 (641.6 eV)[18] and smaller than observed for $La_{0.65}Sr_{0.35}MnO_3$ (642.5 eV),[18,20] $La_{0.65}Ca_{0.35}MnO_3$ (641.8 eV),[18,19] $LaMn^{3+}O_3$ (642.0 eV)[22,23] and $Mn^{4+}O_2$ (642.4 eV)[22,23] but slightly greater than that observed for Mn_2O_3 (641.1 eV), and MnO (640.6 eV).[18] As with the arguments put forward by Choi *et al.*[18] and Taguchi and Shimada,[19] we propose that the Mn $2p$ binding energies for $La_{0.65}Pb_{0.35}MnO_3$ are consistent with a Mn^{3+} state rather than a Mn^{4+} state in the surface region. This assignment is consistent with the fact there is substantial Pb segregation (as discussed later) since Pb is allowed higher oxidation states than the generally expected alkaline earth A^{2+} state (A=Ca, Sr) and this would act to lower the corresponding oxidation state of nearby Mn from 4+ to 3+.

The binding energy of the Pb $4f_{7/2}$ core level increases from 137.8 to 138.2 eV with increasing emission angle as seen in Figs. 2 and 3(b). These binding energies are greater than observed for the Pb^{2+} state seen in PbTe [137.3 eV (Ref. 24)], PbS [137.5 eV (Ref. 24)], and PbO [137.4 (Ref. 25)]. Since the greater the emission angle, the more surface sensitive the x-ray photoemission signal, the higher binding energies for the Pb $4f_{7/2}$ at greater emission angles indicates an effectively higher oxidation of Pb in the surface region consistent with a concomitant lower oxidation of Mn in the surface region. Thus the mixed $Mn^{4+/3+}$ state of the $La_{0.65}A_{0.35}MnO_3$(A=Ca, Sr) materials is suppressed in favor of a Mn^{3+} state in the case of the surface region of $La_{0.65}Pb_{0.35}MnO_3$ as indicated by the core level binding energies of Pb, Mn, and by the Mn core level half width.

The XPS core level data can also be utilized to observe the surface segregation in the manganese perovskites,[8–10] because the effective mean free path of the escaping electrons becomes shorter with increasing emission angle. The data in Fig. 3 show the measured intensity ratio of the Pb to La core

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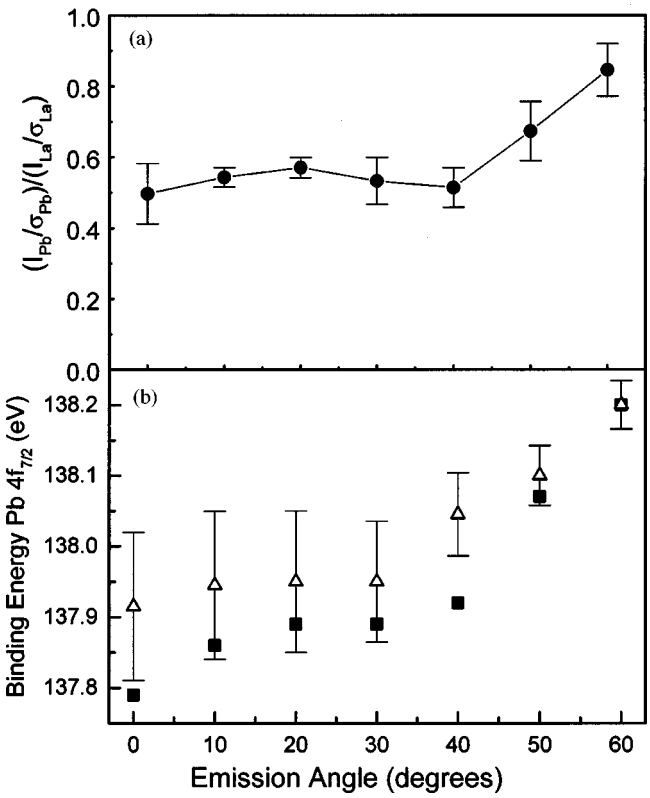

FIG. 3. (a) The emission angle dependence of the x-ray photoemission data. The Pb $4f_{7/2}$ intensity relative to the La $3d_{5/2}$ intensity as a function of emission angle normalized by cross section; (b) the Pb $4f_{7/2}$ binding energy is plotted as a function of emission angle at 300 K (△) and 200 K (■).

level, which increases as a function of the increasing emission angle. Qualitatively this shows that the surface region is Pb rich. In Fig. 3(a) of are several data points taken at different temperatures averaged together. The error bars are quite small and we conclude that the surface segregation profile does not change significantly with temperature between 200 and 300 K.

IV. SUMMARY

Surface segregation in the complex oxides is relatively common and has now been identified in another manganese perovskite. The influence of the surface segregation and surface defects does appear to have some affect upon the core level binding energies and the data suggest that while $La_{0.65}Pb_{0.35}MnO_3$ is MnO_2 terminated, the Mn is in the 3+ state due to corresponding higher oxidation states of Pb in the Pb rich subsurface layer.

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